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Halide-oxide carbon vapor transport of ZnO: Novel approach for unseeded growth of single crystals with controllable growth direction

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ABSTRACT

The thermodynamic analysis of using HCl + CO gas mixture as a chemical vapor transport agent (TA) for ZnO single crystal growth in closed ampoules, including 11 chemical species, is carried out for wide temperature and loaded TA pressure ranges. The advantages of HCl + CO TA for faster and more stable growth are shown theoretically in comparison with HCl, HCl + H_2 and CO. The influence of the growth temperature, of the TA density, of the HCl/CO ratio, and of the undercooling on the ZnO mass transport rate was investigated theoretically and experimentally. The HCl/CO ratios favorable for the growth of *m* planes and (0001)Zn surface were found. It was shown that HCl + CO TA provides: (i) a rather high growth rate (up to 1.5 mm per day); (ii) a decrease of wall adhesion effect and an etch pit density down to 10^3 cm^{-2}; (iii) a minimization of growth nucleus quantity down to 1; (iv) stable unseeded growth of the high crystalline quality large single crystals with a controllable preferred growth direction. The characterization by the photoluminescence spectra, the transmission spectra and the electrical properties are analyzed.

1. Introduction

Zinc oxide (ZnO) crystals have recently drawn attention due to their relatively low price and their application perspectives in optoelectronics [1]. A recent viable direction of application of semiconductor compounds is the fabrication of nanoporous matrices, which give the possibility of obtaining nanowires and nanotubes of various materials as promising structures for optoelectronics and photonics. Manufacturing of such porous materials is possible on the homogeneously doped substrates with controllable high conductive properties [2,3]. One of the cheapest and simple methods of obtaining ZnO crystals with controllable electrical parameters is chemical vapor transport (CVT) in sealed ampoules.

Many reports have been dedicated to the development of unseeded growth technology for ZnO single crystals. Polycrystalline growth is usually observed when C and CO are used as the transport agent (TA) [4,5]. HCl [6], $HgCl_2$ [7], HBr and HI [8] as TAs offer the possibility to grow narrow prismatic crystals with a maximal diameter of about 2 mm. Large unseeded ZnO crystals can be obtained using H_2 [9], but these crystals are usually characterized by structural defects, such as angle boundaries and voids. Furthermore, a strong mechanical contact between crystals and walls of quartz growth ampoules leads to a partial destruction of crystals during the post-growth cooling [9,10]. The most qualitative unseeded single crystals have been obtained with the use of Cl_2+C. However, the growth process for crystals having 1 cm diameter was as long as 40 days [11].

The use of HCl, generating a dense growth medium, favors obtaining void-free n-ZnO seeded single crystals [6]. It can also offer a promising perspective for obtaining crystals homogeneously doped during the growth process, as many metals and oxides effectively interact with HCl. The main disadvantages of HCl are the presence of low angle boundary defects in crystals (the full width at half-maximum of rocking curves (FWHM RC) is 200–300 arcsec), very low growth rate of about 0.2 mm per day at 1050 °C and an undercooling of 60 °C [6]. The last effect is caused by the low temperature dependence of the pressures of the main CVT gaseous species. The development of technology for the simultaneous use of HCl and other TAs, causing a high temperature dependence of the chemical interaction species, can be promising for the increase in growth rate of ZnO. Recently, a new method of using the HCl + H_2 gas mixture was suggested for seeded growth of ZnO [12]. The additional presence of H_2 increases the mass transport rate by 4–7 times, decreases the lateral wall adhesion effect, and raises crystalline quality (FWHM RC is about 100–200 arcsec). The disadvantages of the proposed method

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